

August 1914.

Chemical Series.

Vol. III, No. 8.

Memoirs of the Department of Agriculture in India

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(A) WATER, MAGNESIUM CARBONATE AND
CARBONIC ACID

(B) WATER, CALCIUM CARBONATE, MAGNESIUM
CARBONATE AND CARBONIC ACID

BY

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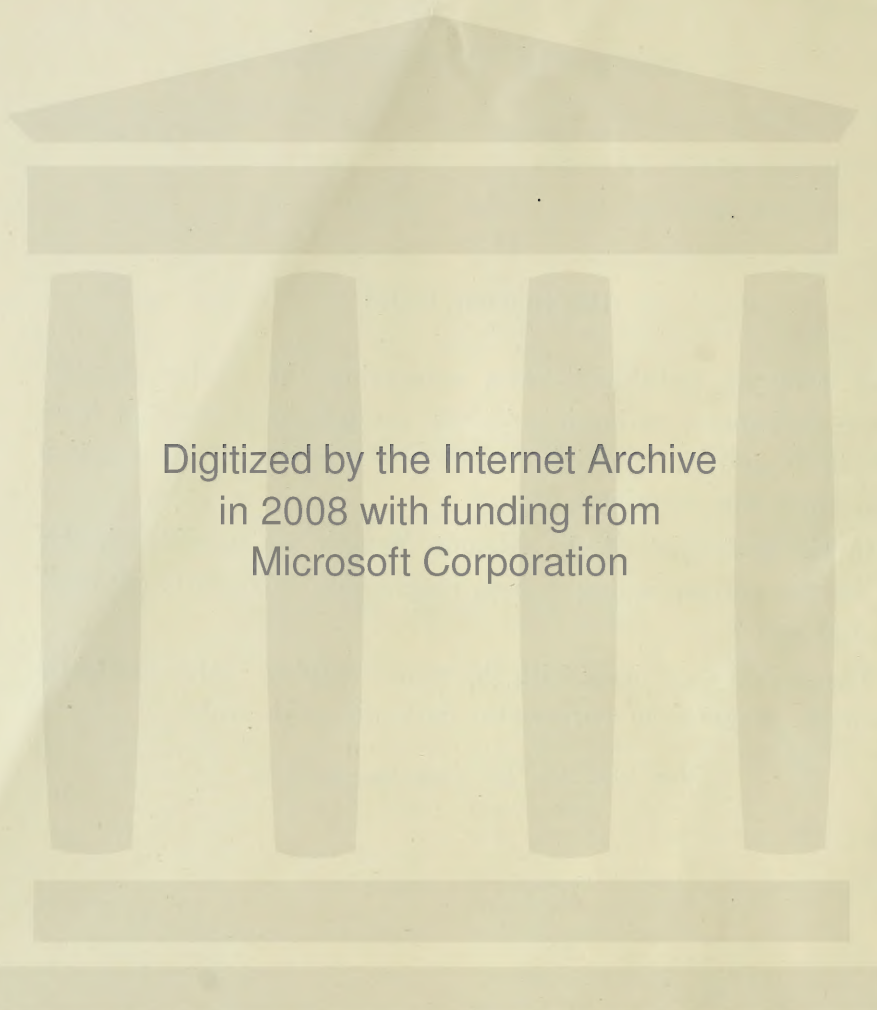
INTRODUCTORY

IN 1909 we published¹ data respecting the system water, calcium carbonate, carbonic acid, at temperatures varying from 20° to 40° C. and for a partial pressure of CO₂ in the gas phase which varied from zero to about 35%.

In the first part of the present Memoir we provide similar data for the corresponding system magnesium carbonate, carbonic acid and water.

The second part deals with the more complex system, calcium carbonate, magnesium carbonate, carbonic acid, water.

¹ *Mem. Dept. Agri. Ind., Chem. Ser., Vol. I, No. 7.*



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PART I.

The system MgCO_3 , CO_2 , H_2O in contact with air.

THE investigation of the system MgCO_3 , CO_2 , H_2O , air, is obviously similar to that of the corresponding CaCO_3 system, but differs from it chiefly by the fact that the magnesium bicarbonate solution is very much more stable and hence requires a much longer period of time to come into equilibrium with the gas phase. It is also very much more soluble in water.

Preparation of pure MgCO_3 , $3\text{H}_2\text{O}$.—Pure magnesium chloride in solution was precipitated by the addition of sodium carbonate, and the magnesium carbonate was washed with CO_2 -free distilled water, until free from sodium, as determined by the flame test. Another method which was adopted during the earlier stages of the work, consisted in dissolving magnesium carbonate or magnesium oxide in water by carbonic acid and agitating the clear solu-

tion of the bicarbonate with air. The precipitated carbonate was again dissolved and precipitated twice. Analysis showed that it consisted of $\text{MgCO}_3, 3\text{H}_2\text{O}$.

Preparation of solution of $\text{Mg}(\text{HCO}_3)_2$.—Magnesium carbonate was agitated with water and carbon dioxide gas in stoppered bottles, the air being first displaced, at room temperature, until the absorption of carbon dioxide ceased. The undissolved carbonate was allowed to settle and the clear solution was drawn off as required.

Method of obtaining equilibrium.—As a consequence of the comparative stability of the bicarbonate, the agitating machine which had been employed in the case of calcium bicarbonate was found to be unsuited to our present purpose. Indeed it was some time before a suitable machine was devised and constructed. For, in order to obtain equilibrium in this system it is necessary to maintain the mixture in a state of rapid agitation for at least a number of days, and at the same time to provide that the total pressure in the apparatus shall be very frequently corrected to that of the atmosphere. For some time bottles containing the solutions, plus gas were rotated on a frame in a large tank of water, but the agitation proved to be too moderate. Finally the apparatus which is illustrated in Figs. I and II was constructed and was found to answer the requirements of the case. Fig. I is a sectional elevation. A is a tank measuring 3 feet by 3 feet by 3 feet filled with water. Its temperature is maintained constant, when above the room temperature by means of a lamp underneath and a Novy's thermo-regulator; when a temperature lower than that of the atmosphere was required, ice was added periodically. A stirrer maintained the water in circulation. The body of water was so large that the temperature of this tank was readily maintained within 0.5°C . of that desired. In the centre of the tank A was a smaller tank, D, measuring $24'' \times 16'' \times 14''$, the upper edge of which was 6'' below that of the large water tank; it was fixed rigidly to the large tank by bolted rods. Inside tank D, a wooden box H, fitted to contain six reaction bottles, was suspended by chains C. C.

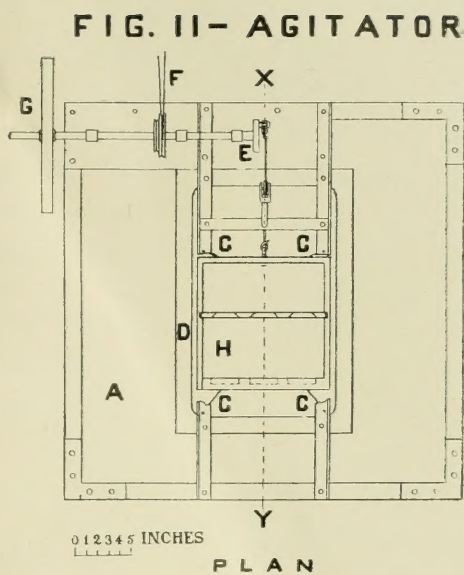
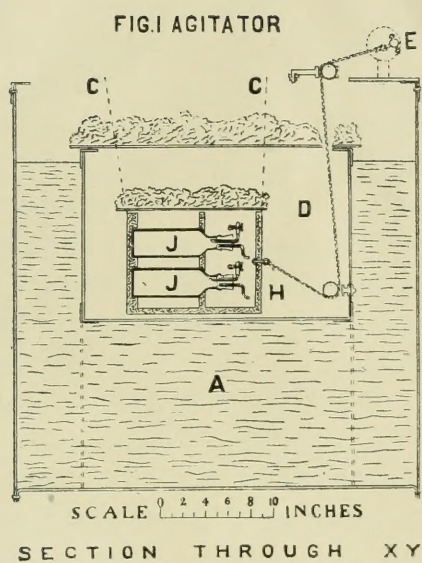
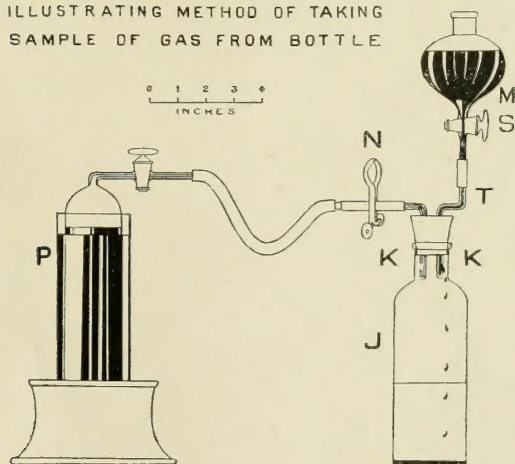


FIG. III
ILLUSTRATING METHOD OF TAKING
SAMPLE OF GAS FROM BOTTLE



(Fig. II) at either end. At the front it was connected by a cord through pulleys to the crank-disc E, and motion to the latter was provided by the belt F from a hot-air engine. G is a fly-wheel to provide for momentum. During one-half of a revolution of the disc E, the cord was tight and drew the box H forward; during the second-half revolution the cord became slack and the box H swung back. The motion given to box H was thus an irregular one, and caused the liquid in the bottles to splash. The agitation was thus as good as though each bottle was shaken by hand. The bottles are illustrated at J in Fig. I and more perfectly in Fig. III. Each was closed by a rubber stopper through which two pieces of manometer tube were passed. These tubes were bent as shown in the figure and that mouth of each tube, which was towards the inside of the bottle, was blown *at the side* of the tube (K. Fig. III). Thus by drawing either tube into the rubber stopper, its mouth became automatically closed. If a tube was pushed into the bottle its mouth communicated with the atmosphere. During the agitation of the bottles in box H, one of the two tubes was drawn into the stopper and remained closed; the other was pushed into the bottle, but was fitted with an india-rubber tube and pinch-cock at the outer end. Hence in order to bring the pressure of the gas inside the bottle into equilibrium with the atmosphere, it was only necessary to open the pinch-cock. It was necessary however to provide that the liquid in the bottle did not cover the end of this tube; the pressure in the bottle was usually initially above that of the atmosphere, and had the bottle contained too much liquid a portion of this would naturally have been ejected when the pinch-cock was compressed. For the first short time after mixing the liquids in the bottles, as detailed below, the bottles were hand-shaken repeatedly so as to allow of the more ready escape of the first and larger portion of the gas.

It will have been noticed that whilst the tank D was immersed in the water of tank A up to near its upper edge, its upper face had to be protected and insulated. In order to provide for this, a thick quilt of cottonwool was placed on the bottles of box H, and

the tank D had a loose wooden cover over which another cotton-wool quilt was spread. Whilst therefore the temperature of the box H could not be expected to coincide exactly with that of the water in tank A, it became very uniform and constant and the temperature of tank A was accordingly regulated so that the temperature in box H became what was desired.

Ascertaining the temperature in box H.—It would not have been sufficiently accurate to place a thermometer in box H and to take it out in order to observe it, for its temperature would have often suffered change in doing so. In order to ascertain this temperature correctly, a small thermometer, graduated to 2°C . was passed through a rubber stopper which fitted a tube of water. This tube of water remained in box H, and, provided it had remained there for a sufficient time to assume the temperature of H, it could be taken out and the thermometer read without the latter suffering any appreciable change of temperature.

We have described this apparatus in detail because we have met with no similar one in the literature.

Method of obtaining suitable mixtures.—The preliminary work on this system although not accurate, had provided approximate information as to the quantity of magnesium carbonate which remains in solution under specified conditions of temperature and CO_2 partial pressure. It was comparatively easy then to place in any bottle that quantity of concentrated magnesium bicarbonate solution and water which would eventually yield a partial pressure of approximately $x\%$ CO_2 . A quantity of precipitated magnesium carbonate was also added. As will be seen from the data on pp. 213-217, the partial pressures at equilibrium were well distributed between the desired limits.

After introducing the measured portion of concentrated bicarbonate solution and the required amount of water together with some precipitated MgCO_3 , the stopper was inserted and the mixture hand-shaken, whereby carbon dioxide was evolved; the clip was therefore opened repeatedly during the period of hand-shaking,

and the latter continued until the evolution of CO_2 gas became negligibly small during short periods of time. The bottle was then placed in the shaking machine. The evolution of CO_2 continued of course for days, but the amount subsequently evolved could be readily released by periodical opening of the pinch-cocks. It was natural that some drops of liquid were always present in the capillary tube N and the movement of these drops served as the indicator of difference of pressure between the gas in the bottle and the atmosphere.

Method of obtaining samples of the liquid and gas phases.—When by repeatedly opening the pinch-cocks of the bottles in the shaking machine it was ascertained that the internal pressure had ceased to change, it was assumed that equilibrium between the three phases had set in. It was naturally necessary, in order to be sure of this, that the temperature had remained constant and also that a sufficient time elapsed between tests. Usually the agitation was continued for at least a full 24 hours after no further alteration of pressure inside the bottle was observed.

It was then necessary to determine the composition of both the liquid and the gas phases. For this purpose the bottle must be removed from the shaking machine without any greater alteration of temperature than could be avoided, and samples of the gas and liquid must be removed without change of composition. To this end the following mode of operating was adopted:—The bottle was removed from the shaking machine and immersed at the tank in a large glass vessel containing water at the same temperature as that of the shaking machine; thus each bottle was subjected to a minimum of exposure to the room temperature.

A sample of the gas was then withdrawn as follows:—(See Fig. III). The exit tube of the Plimpton gas-holder P was filled with mercury and was then connected with the rubber tube of capillary N; the other capillary tube T of the reaction bottle was con-

nected to the mercury reservoir M, the outlet tube of which had been already filled with mercury; the lower end of this capillary T was then pushed into the bottle. On opening the clip N communication was made between the gas in the bottle, and the Plimpton gas-holder, whilst on opening the tap S communication was made between the mercury reservoir and the reaction bottle. Both clip and tap were opened as simultaneously as possible and the flow of mercury was regulated so that the gas could flow into the gas-holder without any great alteration of total pressure in the reaction bottle. It is hardly necessary to mention that any such alteration of pressure would tend to upset the equilibrium between the gas and liquid phases. Immediately after taking this sample of the gas, both the mercury reservoir as also the gas-holder were disconnected from the reaction bottle.

A sample of the filtered liquid was next required. It was in practice impossible to obtain this without exposing the liquid more or less to the atmosphere. Even if it were passed on to an otherwise closed filter successfully, which would not be easy of execution, the filtered liquid would be exposed to ordinary air containing a much lower partial pressure of CO_2 than the liquid had been brought into equilibrium with. On the whole it was considered best, after much consideration and attempts to design specially suitable apparatus, to simply pour the muddy reaction fluid on to a good and large sized paper filter, one working as rapidly as the circumstances of the precipitate would admit, and to depend rather on rapidity of operation, and consequent limit of time, for avoidance of change in the composition of the liquid phase. The fluid was therefore simply poured on to a 15 cm. S.S. "white ribbon" filter paper, the supply being regulated so that the filter remained fairly full whilst the following specimens of filtered liquid were being taken. It may be mentioned that in no case, not even with the more concentrated solutions, was there any perceptible precipitate of MgCO_3 in the filtered liquid until long after the portions had been taken for analysis.

Methods of analysis.—The first 5 to 10 c.c. of the filtrate was discarded. Then a suitable quantity was run directly from the funnel into a weighed Erlenmeyer flask and the stopper inserted. From this portion the amount of total CO_2 was ascertained. Thirdly, another suitable quantity of filtrate was measured by a pipette into a beaker for subsequent titration, from which the amount of base was determined. The closed Erlenmeyer flask was now weighed. The stopper of the Erlenmeyer flask carried a tapped HCl-supply funnel as well as an outlet tube for gas (closed temporarily until attached to the condenser).

Considering the total CO_2 first, sufficient hydrochloric acid was run into the solution to render it acid. The acid liquid was then cautiously raised to a boiling temperature. The outlet tube of the flask had been connected to an inverted condenser, which again was connected to H_2SO_4 drying tubes and soda-lime tubes. The evolved CO_2 was thus expelled from the reaction flask and finally brought into the soda-lime tubes in the usual manner. The “total” CO_2 in the solution taken was thus ascertained.

The other quantity of filtered solution was titrated with standard H_2SO_4 , methyl orange being employed as the indicator, from which the amount of MgCO_3 could be deduced. The equivalent of this quantity is styled “combined” CO_2 and the difference between this and the total CO_2 is styled “free” CO_2 .

In the case of the system CaCO_3 , CO_2 , H_2O the amount of “free” CO_2 is always largely in excess of the “combined” CO_2 and the salt $\text{Ca}(\text{HCO}_3)_2$ even if it really exists, can only do so in the presence of a considerable concentration of H_2CO_3 . The corresponding magnesium salt is however very much more stable and the quantities of “combined” and “free” CO_2 in solution within the limits of pressure and temperature which we have employed are nearly equal. These terms “free” and “combined” CO_2 are merely a convenience.

The sample of gas in the Plimpton gas-holder was analysed for CO_2 in the usual manner.

Mode of expressing the results.—Although the solution of $\text{MgCO}_3 + \text{H}_2\text{CO}_3$ is so nearly one of $\text{Mg}(\text{HCO}_3)_2$ it is simpler for practical purposes to express the concentration of MgCO_3 and CO_2 separately and to calculate each as a function of the partial pressure.

Therefore from the data obtained at each temperature the constants in the expression

$$C^n = k p$$

have been evaluated for MgCO_3 and CO_2 respectively. It was necessary here to bear in mind that MgCO_3 is appreciably soluble in pure water. The published data vary somewhat; Treadwell and Reuter¹ found 19 m. grms., Cameron and Seidell² from 17 to 22 m.grms. per 100 c.c. For our purposes we took 20 m.grms. as being nearly correct. The formula then becomes:—

$$\log [C - 20] = \frac{\log k + \log p}{n}$$

$$C = \text{m. grms. per 100 c.c.}$$

$$p = \% \text{ CO}_2 \text{ in gas phase.}$$

On plotting the constants n and $\log k$ against the temperature it was apparent that there were slight irregularities in them, and that better values would be obtained by assuming that each was a linear function of the temperature. The following final values for temperatures between 20° and 40°C . were then obtained by the method of least squares:—

For MgCO_3 :

$$\log k = 4.24358 - .041049 t$$

$$n = 1.62098 - .0029114 t$$

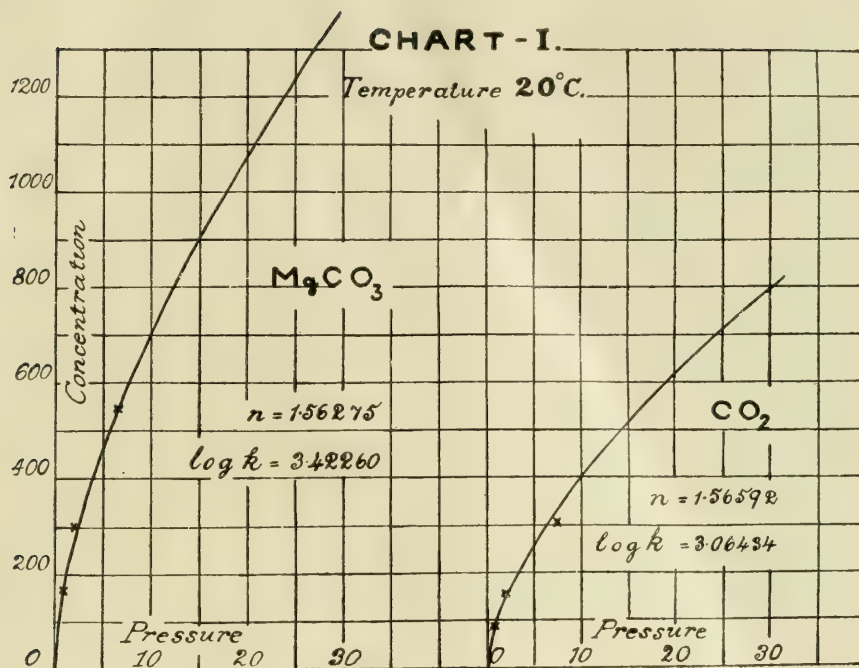
For CO_2 :

$$\log k = 3.44718 - .019142 t$$

$$n = 1.42957 + .0068174 t$$

¹ *Zeits. anorg. Chemie*, 1898, Vol. 17, p. 200.

² *Jour. Phys. Chem.*, 1903, Vol. 7, p. 588.



Temperature 20°C.

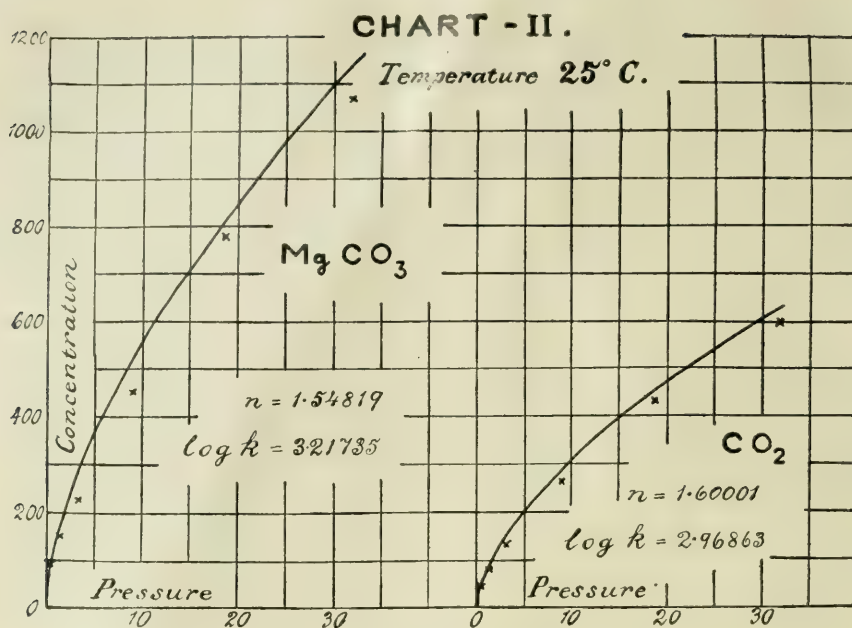
The subjoined statement shows the concentration of MgCO_3 and CO_2 as found and calculated for each experimental partial pressure of CO_2 in the gas phase.

For MgCO_3 , $n = 1.56275$, $\log k = 3.42260$.

„ CO_2 , $n = 1.56592$, $\log k = 3.06434$.

Statement I.

% CO_2 in gas phase.	m. grms. per 100 c.c.				moles $\times 10^3$ per 100 moles water.			
	MgCO_3		CO_2		MgCO_3		CO_2	
	found.	calculated.	found.	calculated.	found.	calculated.	found.	calculated.
·9	165·6	164·8	84·8	84·7	35·5	35·3	34·7	34·6
2·1	302·4	269·1	149·2	145·5	64·8	57·7	61·0	59·5
6·6	544·8	538·3	300·4	302·2	116·8	115·4	122·9	123·6



Temperature 25° C.

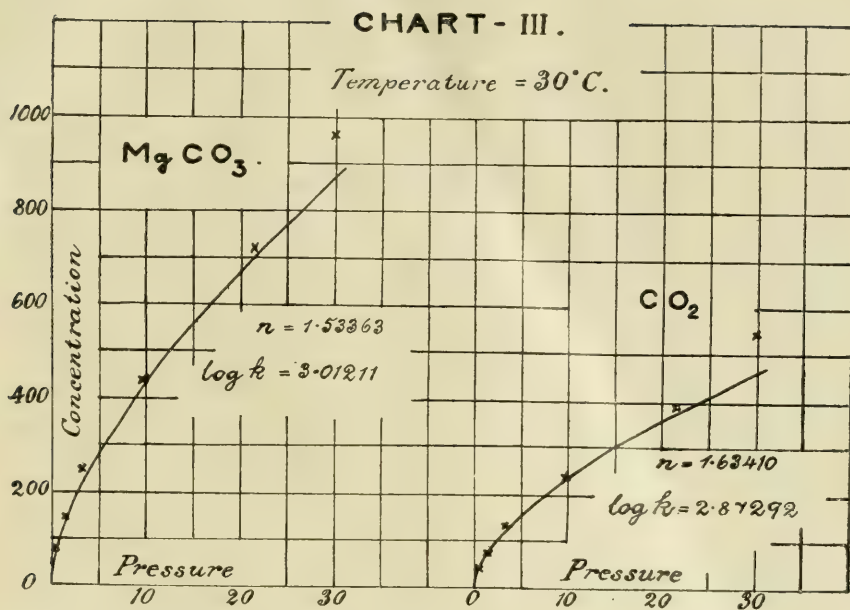
The subjoined statement shows the concentration of MgCO_3 and CO_2 as found and calculated for each experimental partial pressure of CO_2 in the gas phase.

For MgCO_3 , $n = 1.54819$, $\log k = 3.21735$.

„ CO_2 , $n = 1.60001$, $\log k = 2.96863$.

Statement II.

p.	m. grms. per 100 c.c.				moles $\times 10^2$ per 100 moles water.			
	MgCO_3		CO_2		MgCO_3		CO_2	
	found.	calcu- lated.	found.	calcu- lated.	found.	calcu- lated.	found.	calcu- lated.
0.4	88.8	86.2	40.6	40.4	19.0	18.5	16.4	16.5
1.4	147.6	168.8	76.6	88.5	31.6	36.2	31.3	36.2
3.3	232.8	278.9	129.4	151.2	49.9	59.8	52.9	61.8
9.1	451.2	518.4	260.4	285.0	96.7	111.1	106.5	116.6
18.8	775.2	816.4	426.6	448.5	166.1	175.0	174.5	183.4
31.9	1062.0	1140.6	589.8	624.1	227.6	244.4	241.2	255.3



Temperature 30°C.

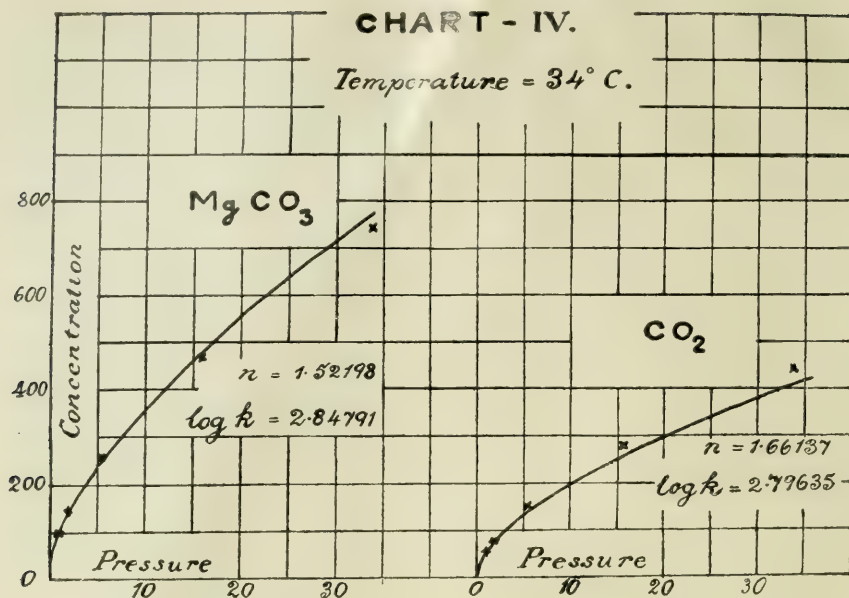
The subjoined statement shows the concentration of MgCO_3 and CO_2 as found and calculated for each experimental partial pressure of CO_2 in the gas phase.

For MgCO_3 , $n = 1.53363$, $\log k = 3.01211$.

„ CO_2 , $n = 1.63410$, $\log k = 2.87292$.

Statement III.

% CO_2 in gas phase.	m. grms. per 100 c.c.				moles $\times 10^5$ per 100 moles water.			
	MgCO_3		CO_2		MgCO_3		CO_2	
	found.	calculated.	found	calculated.	found.	calculated.	found.	calculated.
5	79.2	78.6	40.7	37.5	17.0	16.8	16.7	15.3
1.6	144.0	145.1	75.7	76.4	30.9	31.1	31.0	31.3
3.2	247.2	216.5	132.7	116.7	53.0	46.4	54.3	47.7
9.8	438.0	427.7	238.8	231.6	93.9	91.7	97.7	94.7
21.6	720.0	702.6	387.6	375.6	154.3	150.6	158.5	153.6
30.0	960.0	865.6	543.8	459.2	205.7	185.5	222.4	187.8



Temperature 34°C.

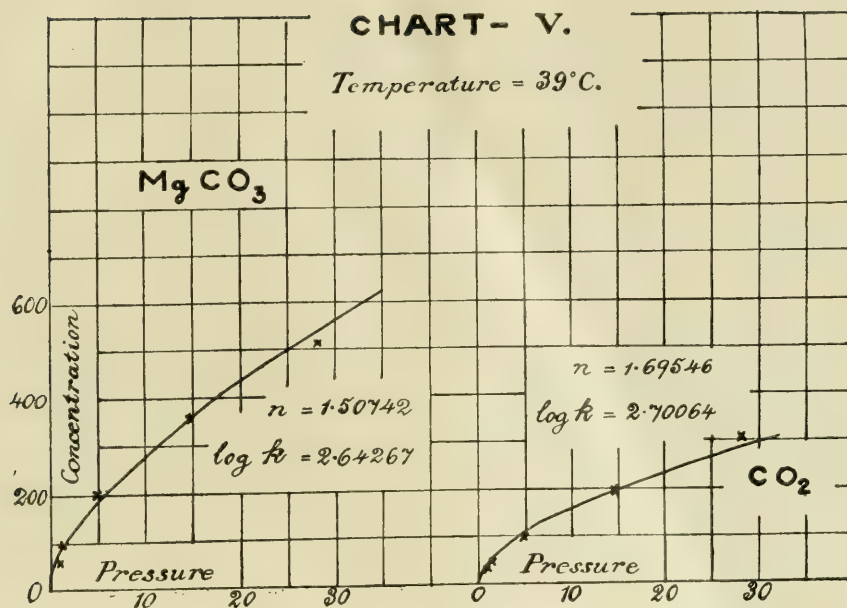
The subjoined statement shows the concentration of MgCO₃ and CO₂ as found and calculated for each experimental partial pressure of CO₂ in the gas phase.

For MgCO₃, $n = 1.52198$, $\log k = 2.84791$.

„ CO₂, $n = 1.66137$, $\log k = 2.79635$.

Statement IV.

p. c _o CO ₂ in gas phase.	m. grms. per 100 c.c.				moles × 10 ³ per 100 moles water.			
	MgCO ₃		CO ₂		MgCO ₃		CO ₂	
	found.	calcu- lated.	found.	calcu- lated.	found.	calcu- lated.	found.	calcu- lated.
1.1	97.2	99.1	52.4	51.1	20.8	21.3	21.4	20.9
1.9	[145.2	133.3	75.9	71.0	31.1	28.6	31.0	29.0
5.5	259.2	247.8	149.4	134.5	55.6	53.1	61.1	55.0
15.9	468.0	477.7	277.5	254.9	100.3	102.4	113.5	104.3
33.9	741.6	772.7	440.6	402.0	158.9	165.6	180.2	164.4
56.8	988.8	1076.5	568.2	548.4	211.9	230.7	232.4	224.3



The subjoined statement shows the concentration of MgCO_3 and CO_2 as found and calculated for each experimental partial pressure of CO_2 in the gas phase.

For MgCO_3 , $n = 1.50742$, $\log k = 2.64267$.

„ CO_2 , $n = 1.69546$, $\log k = 2.70064$.

Statement V.

p.	m. grms. per 100 c.c.				moles $\times 10^3$ per 100 moles water.			
% CO_2 in gas phase.	MgCO_3		CO_2		MgCO_3		CO_2	
	found.	calculated.	found.	calculated.	found.	calculated.	found.	calculated.
1.0	60.0	76.6	34.1	39.2	12.9	16.4	14.0	16.0
1.5	98.4	94.1	41.6	49.7	21.1	20.2	17.0	20.3
4.9	196.8	182.5	96.4	100.0	42.2	39.1	39.4	40.9
14.7	357.6	356.9	191.7	191.1	76.6	76.5	78.4	78.2
28.2	511.2	539.0	300.1	280.7	109.6	115.5	122.7	114.8
50.0	684.0	778.9	409.2	393.5	146.6	166.9	167.4	160.9

*Statement VI.—Calculated concentrations of MgCO_3 and CO_2
(milligrams per 100 c.c.)*

p	20°C		25°C		30°C		34°C		39°C	
% CO_2 in gas phase	MgCO_3	CO_2	MgCO_3	CO_2	MgCO_3	CO_2	MgCO_3	CO_2	MgCO_3	CO_2
5	119.4	58.2	96.5	46.5	78.6	37.5	67.2	31.8	55.8	26.0
10	174.9	90.6	139.7	71.7	112.1	57.3	94.3	48.2	76.6	39.2
20	261.4	141.0	207.3	110.5	164.6	87.6	137.2	73.2	109.7	58.9
30	333.4	182.6	263.4	142.4	208.4	112.2	173.0	93.4	137.4	74.9
40	396.2	219.5	313.1	170.5	247.3	133.8	204.8	111.1	162.1	88.7
50	453.9	253.1	358.5	196.0	282.9	153.4	234.0	127.0	184.7	101.2
100	696.1	394.0	549.7	302.3	433.1	234.5	357.5	192.8	280.9	152.3
150	896.4	510.5	708.3	389.4	558.2	300.5	460.5	246.1	361.4	193.4
200	1073.5	613.4	848.9	466.2	669.2	358.3	552.1	292.6	433.2	229.2
250	1235.2	707.3	977.4	535.9	770.9	410.8	636.2	334.7	499.2	261.4
300	1385.6	794.7	1097.0	600.6	865.7	459.2	714.6	373.5	560.8	291.1

Summary in respect of this system.

1. The concentration of solution of $\text{Mg}(\text{HCO}_3)_2$ in respect of any specified partial pressure of CO_2 is from 5 to 15 times greater than that of the corresponding calcium salt.

2. The ratio of $\text{MgCO}_3 : \text{H}_2\text{CO}_3$ in the solution is much more nearly unimolecular than in the case of the calcium salt; in fact the solution contains only a slight excess of the quantity of H_2CO_3 required by the bicarbonate formula.

3. The solution of $\text{Mg}(\text{HCO}_3)_2$ is much more stable than that of the calcium salt.

4. Regarding the data obtained by others, Engel's¹ were obtained under so much higher pressures of CO_2 — several atmospheres — that they are not comparable with ours. Treadwell and Reuter's² experiments, as was noticed in our memoir³ on the calcium salt, were conducted under such imperfect conditions that supersaturation was to be expected.

¹ Engel and Ville, *Compt. Rend.*, Vol. 93, p. 340; Engel, *Ann. Chim. Phys.*, (6), Vol. 13, p. 349.

² *Zeits. anorg. Chem.*, Vol. 17, p. 200.

³ *Mem. Dept. Agri. Ind., Chem.*, Ser., Vol. I, No. 7.

PART II.

The system CaCO_3 , MgCO_3 , CO_2 , H_2O .

This system has not so far as we are aware been previously examined, though experiments on the action of H_2CO_3 on Dolomites have been made. The latter will be referred to subsequently. The system CaCO_3 , MgCO_3 , CO_2 , H_2O , is naturally very much more complicated than either of those which have been already discussed, and we have been unable to define it at all precisely.

A little consideration shows that if saturated solutions of the two bicarbonates, each in equilibrium with the same partial pressure of CO_2 and at the same temperature, are mixed, a precipitation of CaCO_3 must take place. For although the law of mass action probably would not hold in its entirety, still the *direction* of its effect must be that which this law would indicate. Thus it may not be quite true that the values of the constants

$$K_{\text{Ca}} = \frac{\text{Ca}^{++} \times (\text{HCO}_3')^2}{\text{Ca}(\text{HCO}_3)_2}$$

$$K_{\text{Mg}} = \frac{\text{Mg}^{++} \times \text{HCO}_3')^2}{\text{Mg}(\text{HCO}_3)_2}$$

will be, under the circumstances of a mixture of the solutions of the two salts, identical with those of the individual solutions. But it *is* to be expected that any large increase of HCO_3' ions in the mixed solution would cause a precipitation of Ca^{++} .

A solution of $\text{Mg}(\text{HCO}_3)_2$ saturated for any specified condition of temperature and CO_2 partial pressure is many times more concentrated than that of the calcium salt under like conditions. The

magnesium bicarbonate is not according to Bodländer,¹ nearly so completely hydrolysed as the calcium salt, but after making all allowances for this and other possible modifying influences, it has to be recognised that the concentration of HCO_3^- ions in the magnesium bicarbonate solution must be very much greater than in that of the calcium salt. Hence it follows that mixture of these solutions in equal volumes will cause a precipitation of CaCO_3 .

One or two examples of this effect may be quoted, but before doing so a brief note must be made of the methods employed both for the attainment of equilibrium as also for the analytical determinations.

Attainment of equilibrium.—For some portion of the work the same apparatus was employed as for the magnesium bicarbonate investigation; but later, when it was found that the periods of time required for equilibrium probably extended to weeks, and that large quantities of solution would be required, the reactions were made in winchester bottles maintained in agitation on a revolving frame in a room the temperature of which did not vary by more than 1°C . for long periods. The latter arrangement did not admit of the mixtures being kept at specified temperatures as was readily possible in the former apparatus, but it was the best arrangement available and has yielded much information regarding the system. The materials were placed in the bottles and either a mixture of air and CO_2 gas, previously prepared of specified proportions, passed into the bottle for such a time as would ensure that the gas phase was approximately that desired, or this was done after preliminary agitation. This displacement of the gas phase by a mixture of known composition was performed as frequently (every day, or every several days) as was found to be necessary in order that the composition of the gas phase should remain approximately what was desired. It was therefore necessary to

¹ *Zeits. f. phys. Chemie*, XXXV, p. 27.

sample and analyse the gas phase frequently. Samples were withdrawn by attaching a stopper to the winchester which carried (i) an inlet tube opening in the bottle neck, (ii) an outlet tube opening near the surface of the liquid; the former was attached to the air + CO_2 supply, the latter to the Plimpton gas-holder; hence on opening the connections, a sample of the gas from near the liquid was withdrawn, whilst an equal volume of air + CO_2 was introduced near the stopper. Thus the pressure in the bottle was not materially altered and the gas withdrawn was not materially affected by that which flowed in. The amount of admixture of common air that would necessarily pass into the bottle neck when changing the ordinary stopper for the one carrying the tubes was naturally very small, too small to affect the gas phase materially and could not affect the sample which was withdrawn from a situation some inches below the neck.

Methods of analysis.—The determination of (a) the CO_2 in the gas phase, (b) the total CO_2 in the liquid phase, and (c) the total amount of base present require no explanation; these determinations were conducted in the same manner as when the magnesium salt alone was present. The estimations of CaO and MgO were made as follows:—The 100 c.c. which had been titrated with standard H_2SO_4 for total base, was concentrated to about 20 c.c. and an equal volume of 99% ethyl alcohol was added together with one or two drops of dilute H_2SO_4 . The CaSO_4 was thus precipitated; the length of time required depended on the quantity of lime present; 24 hours was usually sufficient, but when there was less than about 10 m. grms., two days had to be allowed. The calcium sulphate was separated on a Gooch-asbestos filter and weighed as CaSO_4 anhydrous. The error in this determination was about .5 m. grms. The alcoholic filtrate was evaporated cautiously on a sand bath until nearly dry, when the sulphuric acid charred the methyl orange; this residue was extracted with dilute HCl and the MgO was precipitated as phosphate. The error in this determination was about .5 m. grm.

Statement VII.—Data obtained from mixtures of calcium and magnesium bicarbonate solutions.

Examples of mixtures of equal volumes of the solutions.

Volume of $\text{Ca}(\text{HCO}_3)_2$ solution	..	..	100 c.c.	50 c.c.	25 c.c.
Volume of $\text{Mg}(\text{HCO}_3)_2$ solution	..	..	100 c.c.	50 c.c.	25 c.c.
Grams CaCO_3 in solution	..	..	0.0729	0.0364	0.0182
Grams MgCO_3 in solution	..	..	1.5660	0.7830	0.3915
Total volume after diluting with water, if necessary	..	..	200 c.c.	200 c.c.	200 c.c.
Ratio Ca : Mg (molecular equivalents)	..	..	1 : 26	1 : 26	1 : 26
Period of agitation	..	..	7 days	7 days	7 days
Temperature	..	..	29—30°C.	29—30°C.	29—30°C.
p = $^0_{10}$ CO_2 in gas phase after shaking for seven days	..	..	18.0	6.7	2.3
			milligrams per 100 c.c.		
CO_2 in solution—total	..	..	920.1	515.6	335.2
Do. " free "	..	..	524.1	245.9	153.4
Do. " combined "	..	..	396.0	269.7	181.8
Ca in terms of CO_2	..	..	.3	.1	.1
Equal to CaCO_3	..	..	.7	.2	.2
Mg in terms of CO_2	..	..	401.2	274.3	185.1
Equal to MgCO_3	..	..	762.3	521.2	351.7

NOTE.—" Combined " CO_2 is that equivalent to normal carbonates; " free " CO_2 is that in excess of " combined " CO_2 .

In these experiments some CaCO_3 and $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ was added to the mixtures at the commencement in order to have both solid phases present throughout. Although the agitation was stopped before equilibrium had set in, these experiments as well as a number of other similar ones, serve to demonstrate the fact that CaCO_3 becomes practically insoluble in the presence of an excess of $\text{Mg}(\text{HCO}_3)_2$ which is what was expected on theoretical grounds. Some work by Moressee,¹ in which calcium and magnesium oxides were treated with carbonic acid at 5—6 atmosphere pressure, yielded a corresponding result; the solution contained only magnesium carbonate. A like result was obtained by Pattinson.² Following these, a number of experiments were made to ascertain what concentration of $\text{Mg}(\text{HCO}_3)_2$ may be present without causing a precipitation of CaCO_3 .

¹ Cf. Cesaro, *Bull. Acad. Roy. Belg.*, 1910, 234—265; *Abs. Chem. Soc.*, 1910 (ii), 613

² *Chem. News*, 1863, 128.

Statement VIII.

Experiment No.	1	2	3	4	5*	6	7*	8	9*	10	11	12*	13*	14
Gms. CaCO_3 in solution	1.098	1.072	1.098	1.072	1.54	1.543	1.54	1.464	1.54	1.543	1.429	1.54	1.54	1.543
Gms. MgCO_3 in solution	5.535	5.400	3.690	3.690	2.22	2.592	2.33	1.230	1.17	1.296	1.200	0.58	0.55	0.48
Vol. in c.c. (after diluting with water)	1978	1992	1818	1832	216	2200	216	2106	208	2100	2110	204	204	2050
Ratio: $\text{Ca} : \text{Mg}$ (molecular equivalents)	1 : 6	1 : 6	1 : 4	1 : 4	1 : 2	1 : 2	1 : 2	1 : 1	1 : 1	1 : 1	1 : 1	2 : 1	2 : 1	2 : 1
Period of agitation, days	7	7	7	7	8	7	7	7	7	7	7	7	8	7
Temperature	30°	30	30	30	29-30°	30°-31°	29-30	30	29-30°	30°-31°	30°	29-30	29-30°	30-31°
p = % CO_2 in gas phase when agitation stopped	10.6	3.1	11.3	1.5	10.2	6.2	13.2	11.4	11.9	8.5	3.9	12.9	10.8	8.2
milligrams per 100 c.c.														
CO_2 in solution—total	318.2	222.0	220.4	190.6	199.4	120.6	175.9	109.2	146.6	76.4	69.0	92.2	123.7	67.0
Do “ free ”	170.2	82.4	111.0	79.5	97.5	59.0	90.4	70.6	54.6	38.7	37.3	52.2	66.3	39.7
Do “ combined ”	148.0	139.6	109.4	111.1	101.9	61.6	85.5	38.6	92.0	37.7	31.7	40.0	57.4	27.3
Ca in terms of CO_2	N/L	6	N/L	5	N/L	4	1.0	6.8	1.4	5.8	3.5	9.2	2.7	10.8
Equal to CaCO_3	..	1.4	..	1.1	..	..	2.3	15.4	3.2	13.2	7.9	20.4	6.1	24.6
Mg in terms of CO_2	147.5	141.3	100.4	105.5	105.8	63.4	83.0	31.3	90.3	32.5	29.3	32.1	56.3	17.4
Equal to MgCO_3	280.2	268.5	190.8	200.4	201.0	120.5	157.7	59.5	183.0	61.7	55.7	61.0	107.0	33.1

NOTE.—“ Combined ” CO_2 is that equivalent to normal carbonates; “ free ” CO_2 is that in excess of “ combined ” CO_2 .

Of the experiments referred to in this statement Nos. 5, 7, 9, 12 and 13 were conducted in the small bottles and agitating apparatus which were used for the magnesium carbonate system ; the remainder were performed in winchester bottles at room temperature. It is improbable that in any of them a state of equilibrium had set in. but the main result was very definite, namely, that where a higher ratio of magnesium : calcium than 1 : 1 was employed, the latter was substantially all precipitated ; where however the ratio was equal, definite, though small amounts of calcium remained in solution. In the experiments marked with asterisks an excess of CaCO_3 and MgCO_3 was added to the initial mixture ; in all others only the perfectly clear solutions of the bicarbonates were employed. The latter are particularly interesting because not only was a crystalline precipitate formed, but the total amounts of lime and magnesia present in solution at the conclusion of each experiment were determined, and compared with the initially used quantities. These data are as set out in the subjoined statement.

Statement IX.

Experiment No.	Ratio Ca : Mg (molecular equivalents)	CaCO ₃ grms.		MgCO ₃ grms.	
		initial	remaining in solution	initial	remaining in solution
1	1 : 6	1.10	<i>Nil.</i>	5.54	5.59
2	1 : 6	1.07	.03	5.40	5.33
3	1 : 4	1.10	<i>Nil.</i>	3.69	3.73
4	1 : 4	1.07	.02	3.60	3.69
6	1 : 2	1.54	.02	2.59	2.64
10	1 : 1	1.54	.28	1.30	1.30
8	1 : 1	1.46	.33	1.23	1.25
11	1 : 1	1.43	.17	1.20	1.18
14	2 : 1	1.54	.50	.65	.68

There is thus no doubt that the magnesium carbonate remained in solution in every case, whilst the greater part of the calcium carbonate was precipitated. The crystalline precipitates were submitted to the Director of the Geological Survey, who very kindly had them examined. Owing to their minuteness there was some

doubt as to the identity of the crystalline forms, but there was little doubt that the precipitate obtained from mixture of the solutions in the ratio $\text{Ca} : \text{Mg} = 2 : 1$ consisted of calcite, whilst those obtained from higher proportions of Mg were principally aragonite with subordinate quantities of calcite. The chemical analysis showed that the precipitates were in all cases pure CaCO_3 . Regarding the concentrations of the salts in solution, in two instances (Experiments Nos. 2 and 4) the solution contained rather more magnesium carbonate than was to be expected from the partial pressure; each contained a small amount of calcium carbonate, but this fact could not well explain the excess of magnesium salt, which is no doubt due to simple supersaturation. In all other cases the concentration of MgCO_3 was much below what would be expected in the absence of CaCO_3 . In respect of calcium carbonate, the concentration was in every case much below that which would be expected in the absence of MgCO_3 ; in experiments Nos. 12 and 14 the concentrations of CaCO_3 most nearly approach what would be expected from the CO_2 partial pressure, but even in these cases it was little more than one half of what would be present in the absence of MgCO_3 . The amount of "free" CO_2 should have approximated to or have been slightly in excess of the "combined" CO_2 in all cases where all or most of the calcium carbonate had been precipitated, that is in experiments Nos. 1 to 7; in Nos. 2 and 4 the divergence is serious and these are the instances in which the solution was presumably supersaturated with respect to MgCO_3 . In experiment No. 9 also the quantity of "free" CO_2 was materially different from that which might be expected, which may again be an instance of supersaturation with respect to MgCO_3 in the presence of CaCO_3 .

Although these experiments with mixtures of calcium and magnesium bicarbonates were defective in that equilibrium had not set in, they serve the chief end in view, for they demonstrate very definitely that presence of an excess of magnesium carbonate renders calcium carbonate all but insoluble. Experiments Nos. 7,

9, 12 and 13 do not contradict this deduction, because although some magnesium carbonate was originally added to the mixture, it was only a small quantity and presumably all dissolved. Had there been any magnesium carbonate present in the solid phase at the conclusion of the experiments the amount of lime in solution would have been much less. The amount of magnesium carbonate is thus a controlling factor of the solubility of calcium carbonate in the presence of carbonic acid.

The solubility of Dolomite in carbonic acid.

One of the ultimate objects of these investigations had been a more accurate knowledge of the concentration of calcium and magnesium carbonates in the soil-aqueous solution, that is the solution as it actually exists in agricultural land, and it had become apparent that, apart from the presence of salts of other bases or of other salts of magnesium in material quantity, which as a matter of fact is an important restriction, no fertile soil could contain more than very nominal amounts of magnesium carbonate, for the presence of such would render the concentration of dissolved calcium carbonate so low as to interfere with the growth of crops. As an adjunct to this investigation, the effect of carbonic acid on dolomite deserved special consideration. The literature naturally contains many references to this subject.

- (i) Pattinson¹ found that dolomite yielded no MgCO_3 in solution when treated with H_2CO_3 H_2O .
- (ii) Vesterberg,² Bischoff and Gorup-Besanez³ found that dolomite behaves as a true double salt when treated with H_2CO_3 H_2O , though Bischoff also found that in some cases calcite is first removed from dolomitic limestone.
- (iii) Merrill⁴ states that dolomite is much more stable than calcite.

¹ *Chemical News*, 1863, p. 128 ; *Jour. Chem. Soc.*, Abs. 1882, 13

² *Jour. Chem. Soc.*, 1903, Abs., ii, 302.

³ *Jour. Chem. Soc.*, 1872, p. 59.

⁴ " *Rocks and Rock Weathering*," p. 250.

- (iv) Philippi¹ found the calcium carbonate more readily removed than the magnesium salt, and Merrill states that calcareous rocks lose CaCO_3 readily and that dolomite remains.
- (v) Roth² has shown that magnesite is sometimes removed more readily than calcite from dolomitic limestones.

These experiences are generally what one might anticipate. Three cases may be assumed :—

- (a) *Pure dolomite*.—If this is a true double salt as is generally believed, then on treatment with $\text{H}_2\text{CO}_3 + \text{H}_2\text{O}$ the two carbonates would dissolve in equi-molecular proportions and an excess of $\text{Mg}(\text{HCO}_3)_2$ could not occur in the solution so long at least as the conditions of temperature and pressure remained constant. The maximum concentration would be reached when the solution contained the maximum amount of $\text{Ca}(\text{HCO}_3)_2$ which could exist in presence of $\text{Mg}(\text{HCO}_3)_2$ and dolomite.
- (b) *Dolomitic limestone containing calcite*.—If the calcite is more readily soluble in $\text{H}_2\text{CO}_3 + \text{H}_2\text{O}$ than dolomite, then such a limestone would tend to lose calcite and the dolomite would remain, though not necessarily unacted on.
- (c) *Dolomitic limestone containing magnesite*.—A precisely similar argument must hold in this case as in the last. If magnesite is the more soluble, the dolomite would remain, and in this case it could not pass into solution in any material quantity because the presence of $\text{Mg}(\text{HCO}_3)_2$ would prevent any material quantity of $\text{Ca}(\text{HCO}_3)_2$ from being in solution.

¹ *Jour. Chem. Soc.*, 1899, *Abs.*, ii, 306.

² “ *Rocks and Rock Weathering*, ” p. 25.

For our experiments three specimens of dolomite were employed which are designated O, A and B. Specimen O was a white mineral from the neighbourhood of Nagpore; A and B were nearly black minerals which Mr. R. G. Wells of the Tata Iron and Steel Company, Limited, very kindly sent us from Panposh. Their composition was found to be as follows:—

Dolomite.	O	A	B
Insoluble silicates and sand	1.15	2.83	6.35
Oxide of iron, &c. (ammonia ppt.) ..	.86	.49	.66
Lime	29.65	29.06	27.94
Magnesia	22.10	22.11	21.13
Carbonic acid	46.30	45.97	44.22
	100.06	100.46	100.30
Molecular ratio Ca : Mg	1 : 1.036	1 : 1.058	1 : 1.052

Each was pulverised finely and a portion which passed a brass sieve of 90 meshes to the inch was employed.

About 10—20 grms. in each case was placed in a winchester bottle with about 2000 c.c. distilled water and air + CO₂ passed in. The mixture was then agitated on a rotating machine continuously day and night in a room the temperature of which remained very constant. The initial effect of the agitation was naturally a reduction of the partial pressure of CO₂. In order to obtain a specified partial pressure approximately, in any particular case, the required mixture of air + CO₂ was passed into the bottle in sufficient quantity to thoroughly displace that previously present. This alternate procedure of agitation and replacement of the gas phase was continued until the partial pressure of CO₂ remained approximately constant, after which the agitation was continued for some days.

Statement X.—The data thus obtained are set out in the following :—

No. of experiment.	Variety of Dolomite.	Temperature.	Period of agitation, days.	Partial pressure CO_2 % in gas phase.	m. grms. per 100 c.c.		moles $\times 10^3$ per 100 moles H_2O .	
					CaCO_3	MgCO_3	CaCO_3	MgCO_3
1	O	33°	8	4.6	18.4	15.6	3.31	3.34
2	O	31°	6	12.6	20.4	12.9	3.68	2.78
3	O	30°	7	15.3	20.4	12.5	3.68	2.70
4	A	30°	9	6.3	8.6	13.1	1.55	2.82
5	B	30°	9	6.4	11.6	11.4	2.08	2.45
6	O	30°	250	1.3	16.8	12.0	3.02	2.58
7	A	30°	250	1.0	16.1	12.7	2.90	2.74
8	B	30°	250	.5	14.7	11.2	2.66	2.41
9	O	30°	13	4.6	5.9	5.3	1.06	1.15
10	A	30°	13	6.7	10.2	8.4	1.84	1.80

Although the ratio of calcium to magnesium as shown in the last two columns are not precisely 1 : 1 as would be expected for a solution of pure dolomite, they are so nearly so, especially considering the not very perfect conditions employed, that it cannot be doubted that each of these dolomites dissolved as a double salt. There is no evidence that the solution contained generally an excess of either carbonate. The concentrations of the solutions vary and are not proportional to the partial pressure of CO_2 .

In one case, experiment No. 8, the concentration of the $\text{Ca}(\text{HCO}_3)_2$ was approximately that required by the partial pressure of CO_2 and in experiments Nos. 6 and 7 it approached that concentration, thus showing that it is possible at low partial pressures of CO_2 to obtain a solution in contact with dolomite, which approximates to a concentration of $\text{Ca}(\text{HCO}_3)_2$ equal to what would be obtained if calcium carbonate alone were the solid phase. But in all other instances the concentration was very much below this. In respect of $\text{Mg}(\text{HCO}_3)_2$ the concentration of this salt was always far below what it would be if MgCO_3 were the solid phase. Generally, dolomite appears to dissolve as such, but unlike either calcium or magnesium carbonates there is no sign that its solubility increases, above a certain concentration, with increase of partial pressure of CO_2 . The long period of time allowed in these experiments renders this deduction undoubted.

The effect of the presence of (a) CaCO_3 or (b) MgCO_3 with dolomite.—Several experiments were made in which dolomite, plus marble or dolomite, plus $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ were treated with $\text{H}_2\text{CO}_3 + \text{H}_2\text{O}$; other experiments were similarly made in which, to a solution of dolomite in $\text{H}_2\text{CO}_3 + \text{H}_2\text{O}$ and containing an excess of dolomite, CaCO_3 (precipitated) or $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ were added; again, in a third series, dolomite was added to a solution of calcium bicarbonate or magnesium bicarbonate. The data are exhibited in the subjoined statement.

Statement XI.

Experiment No.	Variety of Dolomite.	Temperature.	Period of agitation, days.	Partial pressure CO_2 % in gas phase.	m. grms. per 100 c.c.	
					CaCO_3	MgCO_3
1	O	30°	Dolomite, plus marble.		31.8	9.2
			9	12.5		
2	O	30°	Dolomite, plus $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$.		Nil.	192.8
			9	3.0		
3	O	30°	Dolomite solution.		16.8	12.0
			250	1.3		
4	B	30°	The same after addition of precipitated CaCO_3 .		14.7	11.2
			45	2.0		
			Dolomite solution.			
			250	.5		
5	O	30°	The same after addition of precipitated CaCO_3 .		5.9	5.3
			45	9.8		
			Dolomite solution.			
			13	4.6		
		30°	The same after addition of precipitated CaCO_3 .		19.8	4.6
			4	4.4		

Statement XI—contd.

Experiment No.	Variety of Dolomite.	Temperature.	Period of agitation, days.	Partial pressure CO ₂ % in gas phase.	m. grms. per 100 c.c.	
					CaCO ₃	MgCO ₃
6	A	Dolomite solution.				
		30°	13	6.7	10.2	8.4
		The same after addition of precipitated CaCO ₃				
		30°	4	6.1	28.0	6.9
7	A	Dolomite solution.				
		30°	250	1.0	16.1	12.7
		The same after addition of MgCO ₃ .3H ₂ O				
		30°	28	.6	4.1	20.4
8	A	Dolomite solution.				
		30°	250	1.0	16.1	12.7
		The same after addition of MgCO ₃ .3H ₂ O				
		30°	45	.9	9.5	42.2
9		Calcium bicarbonate solution.				
					40.7	
		The same after addition of dolomite.				
		O	28°	11	10.9	45.5
10		Calcium bicarbonate solution.				
					40.7	
		The same, plus Dolomite and CaCO ₃				
		O	28°	11	11.2	45.9
11		Calcium bicarbonate solution.				
				14.8	50.0	
		The same, plus dolomite.				
		O	25°	9	14.0	45.5
12		Calcium bicarbonate solution.				
					16.2	
		The same, plus dolomite.				
		O	28°	13	1.4	18.4

Statement XI—concl'd.

Experiment No.	Variety of Dolomite.	Temperature.	Period of agitation, days.	Partial pressure CO ₂ % in gas phase.	m. grms. per 100 c.c.	
					CaCO ₃	MgCO ₃
13				..		379.9
	The same, plus dolomite.					
	O	28°	13	10.0	Nil.	379.9
14						352.3
	The same, plus dolomite.					
	O	23°	7	9.0	Nil.	349.6

A consideration of the data of experiment No. 1 shows that the presence of marble does not prevent the carbonic acid attacking the dolomite, though the concentration of Mg (HCO₃)₂ in the solution is distinctly less than we have found in the absence of calcium carbonate. Experiment No. 2 in which a large amount of MgCO₃.3H₂O was present shows how completely this salt prevents the solution of the dolomite, for the amount of Ca(HCO₃)₂ in solution was too small to detect. In other experiments only small amounts of the CaCO₃ or MgCO₃ respectively were added. In Nos. 3 and 4 a comparison of the quantities of CaCO₃ added and subsequently found in solution, showed that all the CaCO₃ had dissolved, whereas in Nos. 5 and 6 there was still a small amount of calcium carbonate in the solid state. There seems to have been in each case a small but measurable precipitation of magnesium carbonate. In experiments Nos. 7 and 8 only small amounts of MgCO₃ were added and in No. 8 the whole dissolved; the corresponding data for No. 7 were not obtained. Finally experiments Nos. 9 to 14 show again that the presence of calcium bicarbonate largely protects dolomite from the solvent action of carbonic acid, whilst magnesium bicarbonate protects it entirely. It is evident then that CaCO₃ will readily dissolve in a solution of dolomite in the

presence of H_2CO_3 , without greatly altering the concentration of the $\text{Mg}(\text{HCO}_3)_2$; on the other hand, when MgCO_3 is dissolved in a solution of dolomite under corresponding conditions, the calcium carbonate of the dolomite becomes precipitated either partly or wholly according to the excess of $\text{Mg}(\text{HCO}_3)_2$ in solution. These experiments confirm fully the anticipations which are set out on page 227.

The "lime-magnesia ratio" in Soils.

Indirectly this investigation offers some explanation of the somewhat contradictory results which have been obtained at experiment stations in different countries regarding the lime-magnesia ratios in soils.

Briefly, these experiments have usually shown that considerable excess of lime, in the form of the carbonate, may be employed without harm, whereas any considerable application of magnesium carbonate has usually proved harmful. Moreover, no fixed proportion of Ca : Mg has been generally found the best, but nearly all experiments show that the proportion of lime should largely exceed that of magnesia.

In the first place, it is to be realised that if, in the soil aqueous solution, there were any calcium sulphate or chloride, either would react with magnesium carbonate.¹ For example, in many experiments magnesium carbonate has been added to soils to which fertilisers, *e.g.*, ammonium salts or superphosphate have also been added, and in such cases more or less of the magnesium carbonate must have been changed to a more soluble salt, but unchanged magnesium carbonate must also have tended to render calcium carbonate insoluble. In the case of dolomitic limestone, the solubility of the calcium carbonate would probably not be reduced sufficiently to affect plant growth and this explains why such limestone has frequently proved serviceable. But where magnesium carbonate has been employed in any large quantity, its presence

¹ Bottomley, *Jour. Chem. Soc., Trans.*, 1893, p. 696.

in the soil might easily reduce the solubility of calcium carbonate sufficiently to cause "lime-starvation."

Summary in respect of the system CaCO_3 , MgCO_3 , H_2CO_3 , H_2O .

1. If a mixture of calcium and magnesium carbonates is subjected to the action of carbonic acid and water, the calcium carbonate is largely or wholly prevented from dissolving, a fact which is in accordance with the indication of the law of mass action.

2. Dolomite has been found by us, as by others, to dissolve in carbonic acid as such, but so far as we could ascertain the concentration does not depend only on that of the carbonic acid.

3. Dolomite is protected from the action of carbonic acid to a great extent by the presence of calcium carbonate, and magnesium carbonate protects it completely.

4. The addition of calcium carbonate to a solution of dolomite in presence of excess of carbonic acid seems to cause a slight precipitation of magnesium carbonate, but no explanation of this can be offered.

5. If magnesium carbonate is added in any material quantity to agricultural land, it may readily cause an almost entire precipitation of calcium carbonate and hence render the soil infertile. This fact probably explains in part the crop failure which has so often accompanied the application of magnesium carbonate to land in experiments on Loew's "lime-magnesia ratio."

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